Thermochimica Acta 660 (2018) 11–17

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Analysis of solute-pyridine intermolecular interactions based on experimental enthalpies of solution and enthalpies of solvation of solutes dissolved in pyridine

Mikhail A. Varfolomeev[a,*], Mikhail A. Stolov[a], Ruslan N. Nagrimanov[a], Ilnaz T. Rakipov[a], William E. Acree Jr.[b], Michael H. Abraham[c]

[a] Department of Physical Chemistry, Kazan Federal University, Kremlevskaya 18, Kazan, 420008, Russia
[b] Department of Chemistry, 1155 Union Circle # 305070, University of North Texas, Denton, TX, 76203-5017, USA
[c] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK

ARTICLE INFO

Keywords:
Pyridine
Multi-parameter correlation
Hydrogen bond
Solution calorimetry
Enthalpy of solvation

ABSTRACT

In present work thermochemistry of solvation of inert gases and organic solutes in pyridine was thoroughly studied using solution calorimetry technique. Enthalpies of solution at infinite dilution of 21 organic solutes were determined experimentally at 298.15 K. Measured and literature data were analyzed using Acree and Abraham multi-parameter correlations for description of enthalpies of solvation. Both hydrogen bonding enthalpies between solute and pyridine in bulk pyridine and Gibbs energies of 1:1 complexation between solute and pyridine were calculated using solute and solvent descriptors. Obtained results are in good agreement with values calculated by previously proposed methods.

1. Introduction

Thermochemical properties of solutes dissolved in organic solvent media provide valuable information regarding solute-solvent and solvent–solvent interactions that can be exploited in designing more efficient organic synthetic methods and chemical separation processes. Activity coefficients can be used to calculate solubilities of starting reactants, synthesized products and reaction by-products in organic solvents. Solubility data allows one to select solvent reaction media to increase product yields and to facilitate isolation of the desired product from any unreacted starting materials or reaction bi-products that may have been formed during the course of the chemical reaction. Activity coefficients can also be used to design extraction, distillation and recrystallization processes that might be needed to remove unwanted impurities from the synthesized organic compound. Enthalpies of solution and enthalpies of solvation data allow one to extrapolate measured and predicted solubility and activity coefficient data to slightly higher or lower temperatures. Such extrapolations are often needed in optimizing experimental conditions to maximize product yield and minimize manufacturing cost. Jalan et al. [1] discussed the importance of solvation energies and solvation enthalpies in quantitatively predicting solution-phase chemical kinetics. Also, if we consider chemical reaction in any solvent in the view of energy of this process, solvation effect should be taken into account, because thermodynamic functions of solvation $\Delta_{solv}f^{A/S}$ (enthalpy, entropy and free Gibbs energy) of initial compounds and products will be different. Generally, thermodynamic functions of solvation of solute A in any solvent S can be found from experimentally measured values of thermodynamic functions of solution in the same solvent according to Eq. (1).

$$\Delta_{solv}f^{A/S} = \Delta_{soln}f^{A/S} - \Delta^{g}_{cr,l}f^{A} \quad (1)$$

where $\Delta^{g}_{cr,l}f^{A}$ is a thermodynamic function of vaporization (for liquid sample at 298.15 K) or sublimation (for solid sample at 298.15 K) of solute A.

Our contributions in studying the thermodynamic properties of solutes dissolved in organic solvents are two-fold. First, we have published infinite dilution activity coefficient [2–7] and solubility data [4–9], as well as enthalpy of solution data [2,3,10–17], for a wide range of organic solutes dissolved in organic solvents of varying polarity and hydrogen-bonding character. Second, we have used our measured values to develop mathematical correlations for describing solute transfer between two condensed phases and solute transfer into condensed phases from the gas phase. Our derived correlation equations and solution models provide very accurate mathematical descriptions of the observed transfer properties, and contain terms for describing solute-solvent and solvent–solvent interactions. In earlier papers we have

* Corresponding author at: Department of Physical Chemistry, Kazan Federal University, Kremlevskaya 18, 420008 Kazan, Russia.
E-mail addresses: vma.ksu@gmail.com, mikhail.varfolomeev@kpfu.ru (M.A. Varfolomeev).

https://doi.org/10.1016/j.tca.2017.12.016
Received 9 July 2017; Received in revised form 9 December 2017; Accepted 12 December 2017
Available online 13 December 2017
0040-6031/ © 2017 Elsevier B.V. All rights reserved.